

Nonlinear screening of charged macromolecules

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We present several aspects of the screening of charged macromolecules in an electrolyte. After a review of the basic mean field approach, based on the linear Debye–Hückel theory, we consider the case of highly charged macromolecules, where the linear approximation breaks down and the system is described by full nonlinear Poisson–Boltzmann equation. Some analytical results for this nonlinear equation give some interesting insight on physical phenomena like the charge renormalization and the Manning counterion condensation.

Keywords: Colloids, electrolytes, nonlinear Poisson–Boltzmann equation

1. Introduction and the linear Poisson–Boltzmann equation

A colloidal suspension is a system composed of two substances, one dispersed into the other. The dispersed phase is composed of macromolecules, with size of the order 10^{-8} m – 10^{-6} m, while the dispersion medium, or continuous medium, is composed of small micromolecules, and/or microions, with size of the order of the nanometer. Of particular interest are the charge-stabilized colloids, where the dispersed macromolecules have ionizable sites and, when immersed into the dispersion medium, they acquire a surface electric charge which ensures repulsion between them and thus allows the colloid to stabilize and prevents aggregation.

Since the length and time scales of the microcomponents of the dispersion medium are much smaller than the ones of the dispersed phase, it is convenient to average over the degrees of freedom of the dispersion medium and treat the system as a one-component system composed by the macromolecules which interact via an effective potential. To understand the physical and thermodynamical properties of these systems, it is important to determine this effective interaction between the macromolecules, which results not only from the direct interaction between the macromolecules, but also the interaction mediated by the microions of the dispersion medium.

The basic theory to find this effective interaction for charge-stabilized colloid was developed independently by [Derjaguin and Landau 1941], and [Overbeek and Verwey 1948], and it is known as the DLVO theory. It is based on the work of [Debye and Hückel 1923]. Let us consider a spherical charged macromolecule, with radius a , and charge Ze (e is the elementary charge) immersed in an electrolyte with positive microions of charge z_+e and average density n_+ , and negative microions of charge $-z_-e$ and average density n_- . Without loss of generality we can suppose $Z > 0$. [Debye and Hückel 1923] idea is to treat the microions in a mean field approximation: at temperature T , the local density of microions of charge $q_{\pm} = \pm z_{\pm}e$ at a distance r from the macro-

molecule can be approximated by

$$n_{\pm}(r) = n_{\pm} e^{-\beta q_{\pm} \Psi(r)}, \quad (1.1)$$

where $\Psi(r)$ is the electrostatic potential, and $\beta = 1/(k_B T)$, with k_B the Boltzmann constant. Replacing this into Poisson equation of electrostatics yield the Poisson–Boltzmann equation

$$\Delta \Psi = -\frac{4\pi e}{\epsilon} (z_+ n_+ e^{-\beta e z_+ \Psi} - z_- n_- e^{\beta e z_- \Psi}), \quad (1.2)$$

where ϵ is the dielectric constant of the dispersion medium.

It is convenient to introduce the following notations: the reduced potential $y = \beta e \Psi$, the Bjerrum length $l_B = \beta e^2 / \epsilon$, the Debye length $\kappa^{-1} = (4\pi l_B (z_+^2 n_+ + z_-^2 n_-))^{-1/2}$. With these notations, Poisson–Boltzmann equation reads

$$\Delta y = \frac{\kappa^2}{z_+ + z_-} [e^{z_- y} - e^{-z_+ y}]. \quad (1.3)$$

If the electrostatic coupling between the macromolecule and the microions is small, $y(r) \ll 1$, for any distance r , the nonlinear Poisson–Boltzmann equation (1.3) can be linearized to obtain

$$\Delta y = \kappa^2 y. \quad (1.4)$$

For an impenetrable spherical macromolecule with uniform surface charge (total charge Ze and radius a), the solution of this equation is the DLVO potential

$$y(r) = Z l_B \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r}. \quad (1.5)$$

From this equation, one can see that $1/\kappa$ is the screening length.

It is also interesting to consider the case of cylindrical macromolecules, for instance stiff polyelectrolytes, ADN, etc. As a first approximation, for an infinitely long cylinder with radius a and linear charge density e/ℓ , uniformly spread over its surface, the solution of equation (1.4) gives the electrostatic potential at a radial distance r from the cylinder

$$y(r) = \frac{2\xi}{\hat{a} K_1(\hat{a})} K_0(\hat{r}), \quad (1.6)$$

where K_0 and K_1 are the modified Bessel functions of order 0 and 1. We have defined the reduced linear charge density of the cylinder $\xi = l_B/\ell$, and it is convenient to measure the distances in Debye length units: $\hat{r} = \kappa r$ and $\hat{a} = \kappa a$. The boundary conditions that complement the differential equation (1.4) to yield the solution (1.6) are

$$\lim_{r \rightarrow a} r \frac{dy}{dr} = -2\xi, \quad \text{and} \quad \lim_{r \rightarrow \infty} \nabla y(r) = 0. \quad (1.7)$$

It should be noticed that at large distances from the cylinder, compared to the Debye length, the potential exhibits again an exponential decay, as for the case of spherical macromolecules,

$$y(r) \sim \frac{2\xi}{\hat{a} K_1(\hat{a})} \sqrt{\frac{\pi}{2\kappa r}} e^{-\kappa r}, \quad r \gg \kappa^{-1}. \quad (1.8)$$

In the following sections, we turn our attention to the case of highly charged macromolecules, where the linear approximation breaks down and the full nonlinear equation (1.3) should be used. Several nonlinear effects appear, which we will review. In section 2, we study the nonlinear phenomenon known as the charge renormalization [Alexander et al. 1984, Trizac et al. 2002], which is generic, both for the spherical and cylindrical geometries. In section 3, we focus our attention on the cylindrical case, where an analytical solution of the nonlinear Poisson–Boltzmann equation is available. From the analysis of this analytic solution we discuss the phenomenon of counterion condensation.

2. Charge renormalization

For a highly charged macromolecule, Poisson–Boltzmann equation (1.3) cannot be linearized near the macromolecule surface. However, due to the screening effect, the potential will decay and become small, $|y(r)| \ll 1$, at large distances from the macromolecule surface, $r - a \gg \kappa^{-1}$. In that far region, the linear version (1.4) of Poisson–Boltzmann equation holds. Then, for a spherical macromolecule, the potential will behave as

$$y(r) \sim A \frac{e^{-\kappa r}}{r} \quad (2.1)$$

at large distances from the macromolecule. To find the constant of integration A , one needs to enforce the boundary condition at the surface of the macromolecule that the normal component of the electric field is proportional to the surface charge density. However, the form (2.1) of the potential is not valid in that close region. One needs to find also the form of the potential close to the macromolecule surface, and connect it to the large-distance behavior (2.1) to find explicitly the integration constant A . In analogy to the linear solution (1.5), one can write the $A = Z_{\text{ren}} l_B e^{\kappa a} / (1 + \kappa a)$, defining a renormalized charge Z_{ren} . The large-distance behavior of the potential then takes a DLVO familiar form

$$y(r) \sim Z_{\text{ren}} l_B \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r}, \quad (2.2)$$

but replacing the bare charge Z of the macromolecule by the renormalized one Z_{ren} . In the cylindrical geometry, the renormalized charge concept also applies. In that case, the large-distance behavior of the potential is

$$y(r) \sim \frac{2\xi_{\text{ren}}}{\hat{a}K_1(\hat{a})} K_0(\hat{r}), \quad (2.3)$$

with a renormalized linear charge density ξ_{ren} . The determination of the renormalized charge requires knowledge of the short-distance behavior of the solution of the nonlinear Poisson–Boltzmann equation (1.3). This can be done numerically, as in the original work of [Alexander et al. 1984]. In experimental situations, the unknown renormalized charge is often taken as an adjustable fitting parameter. There are also analytical approaches to find the renormalized charge [Trizac et al. 2002, Shkel et al. 2000, Téllez and Trizac 2004], mostly based on approximations using the solution to the nonlinear Poisson–Boltzmann equation in the planar case.

Let us illustrate the concept of charge renormalization in the planar geometry where an explicit solution for the nonlinear Poisson–Boltzmann equation is

known [Gouy 1910, Chapman 1913]. The system is an infinite charged plane, with charge density $\sigma > 0$, immersed in an electrolyte, which, for simplicity, we consider symmetric $z_+ = z_- = 1$. Let Ox be the axis perpendicular to the plane, which we suppose located at $x = 0$, the electrolyte occupies the region $x > 0$. The nonlinear Poisson–Boltzmann equation in this situation reads

$$\frac{d^2 y(x)}{dx^2} = \kappa^2 \sinh y(x). \quad (2.4)$$

It can be integrated once by multiplying by dy/dx ,

$$\frac{dy(x)}{dx} = -2\kappa \sinh \frac{y(x)}{2}. \quad (2.5)$$

where the boundary condition $dy/dx \rightarrow 0$ when $x \rightarrow \infty$ has been used. This last equation is separable and can be integrated, finally obtaining

$$y(x) = 2 \ln \frac{1 + Ae^{-\kappa x}}{1 - Ae^{-\kappa x}}. \quad (2.6)$$

Where A is a constant of integration, which is found using the boundary condition at the surface of the charged plane

$$\frac{dy}{dx}(0) = -4\pi l_B \sigma / e. \quad (2.7)$$

Notice that at large distances from the plane, $\kappa x \gg 1$, the potential behaves as

$$y(x) \sim 4Ae^{-\kappa x}. \quad (2.8)$$

This is the expected behavior for the linear version of Poisson–Boltzmann equation in this geometry $y''_{\text{lin}}(x) - \kappa^2 y_{\text{lin}}(x) = 0$. The linear solution is $y_{\text{lin}}(x) = 4\pi l_B \sigma e^{-\kappa x} / (e\kappa)$. Comparing to the large-distance behavior of the nonlinear solution (2.8), one can define the renormalized surface charge density σ_{ren} , by writing the constant of integration A as

$$A = \pi l_B \sigma_{\text{ren}} / (e\kappa). \quad (2.9)$$

Then, the large-distance behavior of the potential is

$$y(x) \sim \frac{4\pi l_B \sigma_{\text{ren}}}{e\kappa} e^{-\kappa x}. \quad (2.10)$$

To find explicitly the renormalized charge, one needs to apply the boundary condition (2.7) at the surface of the charged plane. For this, one needs the short-distance behavior of the potential. From the explicit solution (2.6), we find

$$y(x) = 2 \ln \frac{1 + A}{1 - A} - \frac{4Ax}{1 - A^2} + O(x^2), \quad (2.11)$$

when $x \rightarrow 0$. Using this, we apply the boundary condition (2.7) to find

$$\frac{A}{1 - A^2} = \frac{\pi \sigma l_B}{e\kappa}. \quad (2.12)$$

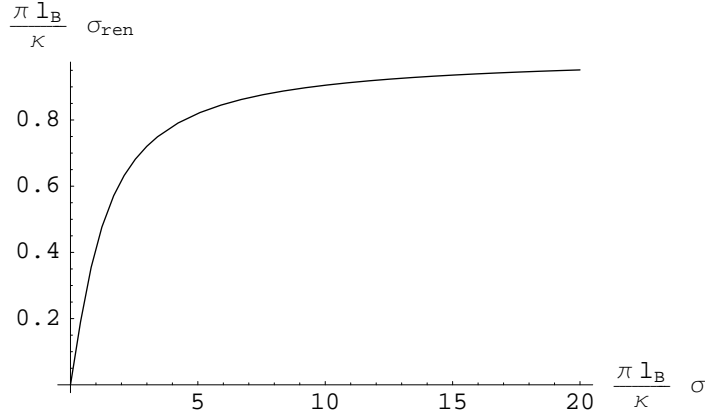


Figure 1. Renormalized charge as a function of the bare charge in the planar case, for a symmetric electrolyte.

Solving, and using (2.9), we find the renormalized surface charge

$$\hat{\sigma}_{\text{ren}} = \frac{\sqrt{\hat{\sigma}^2 + 1} - 1}{\hat{\sigma}}, \quad (2.13)$$

where we have defined reduced charge densities $\hat{\sigma} = \pi l_B \sigma / (e\kappa)$ and $\hat{\sigma}_{\text{ren}} = \pi l_B \sigma_{\text{ren}} / (e\kappa)$.

Figure 1 shows a plot of the renormalized charge as a function of the bare charge. Notice the saturation effect: when $\sigma \rightarrow \infty$, the renormalized charge approaches a finite value $\hat{\sigma}_{\text{ren}} \rightarrow 1$. This saturation effect can also appear in other theories obtained by modification of Poisson–Boltzmann equation using a density functional formulation [Téllez and Trizac 2003]. In that saturation regime, the large-distance behavior potential becomes independent of the bare charge of the plane

$$y_{\text{sat}}(x) \sim y_0 e^{-\kappa x} = 4e^{-\kappa x}. \quad (2.14)$$

The value $y_0 = 4$ plays an important role. It can be seen as an effective surface potential for the plane, if one wants to match the linear solution of Poisson–Boltzmann equation with the nonlinear one in the close vicinity of the highly charged plane. This is also the starting point to find the renormalized charge at saturation for highly charged macromolecules of arbitrary shape. For these macromolecules, when they are highly charged, the linear Poisson–Boltzmann equation can be solved with an effective boundary condition of constant surface potential y_0 , to find the behavior of the potential at large distances and the corresponding renormalized charge, as explained in [Bocquet et al. 2002]. For instance, for a spherical macromolecule, the solution of the linear Poisson–Boltzmann equation with the effective constant potential boundary condition at the surface of the macromolecule $y(a) = y_0 = 4$, is

$$y_{\text{sat, sphere}}(r) = y_0 e^{\kappa a} a \frac{e^{-\kappa r}}{r}. \quad (2.15)$$

The nonlinear solution, at large distances has the behavior given by equation (2.2). Comparing both equations (2.2) and (2.15), we find an approximate value for the

renormalized charge in the saturation regime

$$Z_{\text{ren}}^{\text{sat}} = \frac{a}{l_B} y_0 (\kappa a + 1) = \frac{a}{l_B} (4\kappa a + 4). \quad (2.16)$$

This approximation is based on the planar solution of the nonlinear Poisson–Boltzmann equation, and therefore it is accurate for large macromolecules with $\kappa a \gg 1$, and only at the first order in κa . One can improve this estimate by developing a planar expansion of the solution of the spherical geometry, as done in [Shkel et al. 2000, Trizac et al. 2003, Téllez and Trizac 2004]. Up to terms of order $O(1/(\kappa a))$, the renormalized charge at saturation for spheres in a 1:1 electrolyte is [Trizac et al. 2003]

$$Z_{\text{ren}}^{\text{sat}} = \frac{a}{l_B} (4\kappa a + 6). \quad (2.17)$$

The starting point to obtain estimates of the renormalized charge at saturation is the value y_0 of the effective surface potential at saturation in the planar geometry. This depends only on the constitution of the electrolyte. We propose now a simple formula that gives y_0 in the generic case of a multicomponent electrolyte, composed of several species of ions with charges $\{q_\alpha e\}$ and densities $\{n_\alpha\}$. The nonlinear Poisson–Boltzmann equation in the planar geometry reads now

$$y''(x) + 4\pi l_B \sum_{\alpha} q_{\alpha} n_{\alpha} e^{-q_{\alpha} y(x)} = 0. \quad (2.18)$$

Multiplying by $y'(x)$ this equation, it can be integrated once to find

$$(y'(x))^2 = 8\pi l_B \sum_{\alpha} n_{\alpha} (e^{-q_{\alpha} y(x)} - 1), \quad (2.19)$$

where the boundary condition $y'(x) \rightarrow 0$ when $x \rightarrow \infty$ has been used. Introducing the inverse Debye length $\kappa = (4\pi l_B \sum_{\alpha} q_{\alpha}^2 n_{\alpha})^{-1/2}$, one obtains the formal solution

$$\kappa x = \int_{y(x)}^{y(0)} \frac{du}{\sqrt{\frac{2}{\sum_{\alpha} q_{\alpha}^2 n_{\alpha}} \sum_{\alpha} n_{\alpha} (e^{-q_{\alpha} u} - 1)}}. \quad (2.20)$$

Suppose the charged plane is located at $x = 0$ and positively charged, and we are in the saturation regime, therefore $y(0) \rightarrow +\infty$. At large distances from the plane, $\kappa x \gg 1$, the potential behaves as $y(x) \sim y_0 e^{-\kappa x}$, thus $\kappa x = \ln y_0 - \ln y(x) + o(\ln y(x))$ as $y(x) \rightarrow 0$. Replacing in (2.20) we find

$$\begin{aligned} \ln y_0 &= \lim_{y \rightarrow 0} \left[\int_y^{\infty} \frac{du}{\sqrt{\frac{2}{\sum_{\alpha} q_{\alpha}^2 n_{\alpha}} \sum_{\alpha} n_{\alpha} (e^{-q_{\alpha} u} - 1)}} + \ln y \right] \\ &= \text{Pf.} \int_0^{\infty} \frac{du}{\sqrt{\frac{2}{\sum_{\alpha} q_{\alpha}^2 n_{\alpha}} \sum_{\alpha} n_{\alpha} (e^{-q_{\alpha} u} - 1)}}. \end{aligned} \quad (2.21)$$

Thus, the value of y_0 is expressed as a Hadamard finite part (Pf.) of the integral (2.21). Alternatively, it can be computed from

$$\ln y_0 = \int_0^1 \left[\frac{1}{\sqrt{\frac{2}{\sum_{\alpha} q_{\alpha}^2 n_{\alpha}} \sum_{\alpha} n_{\alpha} (e^{-q_{\alpha} u} - 1)}} - \frac{1}{u} \right] du + \int_1^{\infty} \frac{du}{\sqrt{\frac{2}{\sum_{\alpha} q_{\alpha}^2 n_{\alpha}} \sum_{\alpha} n_{\alpha} (e^{-q_{\alpha} u} - 1)}}. \quad (2.22)$$

Table 1. Value of the saturation potential for several electrolytes.

$z_+ : z_-$	1:5	1:4	1:3	1:2	1:1	2:1	3:1	4:1	5:1
y_0	0.56080	0.71742	0.99388	1.6077	4	6	8.7070	12.314	17.337
$z_+ : z_-$	2:3	3:2	2:5	5:2		3:5	5:3	1:10	10:1
y_0	1.1542	2.4611	0.61471	3.6270		0.67242	1.7544	0.26761	70.337

In the case of a two-component electrolyte $q_1 = z_+$ and $q_2 = -z_-$, the saturation value y_0 can be expressed as a function of the ratio $r = z_+/z_-$,

$$y_0 = \frac{1}{z_-} \exp \left[\text{Pf.} \int_0^\infty \sqrt{\frac{r}{2}} \frac{du}{\sqrt{\frac{e^{-ru}}{1+r} + \frac{e^u}{1+r^{-1}} - 1}} \right]. \quad (2.23)$$

In the cases of electrolytes with $z_+ : z_-$ equal to 1:1, 1:2, and 2:1, the integral can be computed exactly to find the known values [T  lez and Trizac 2004], $y_0^{1:1} = 4$, $y_0^{1:2} = 6(2 - \sqrt{3}) \simeq 1.6077$, and $y_0^{2:1} = 6$. Table 1 gives the value of the saturation potential for other electrolytes.

3. Cylindrical macromolecules

(a) Exact solutions for Poisson–Boltzmann equation and the connection problem

In this section, we focus our attention on the study of the screening of a thin cylindrical macromolecule, with radius $a \ll \kappa^{-1}$. Besides the charge renormalization effect, another interesting phenomenon that occurs in this geometry is the counterion condensation. This was first realized by Onsager and studied by [Manning 1969] and [Oosawa 1971]. To understand this phenomenon, consider the Boltzmann factor between the macromolecule and an ion of opposite charge (counterion): $\exp(-2z_- \xi \ln r) = r^{-2z_- \xi}$. It diverges when $r \rightarrow 0$, and furthermore it is not integrable near $r \rightarrow 0$ if $\xi > 1/z_-$. This means that, for an infinitely thin macromolecule, with radius $a = 0$, the thermodynamics are not properly defined unless $\xi < 1/z_-$. In real situations $a \neq 0$. For $\kappa a \ll 1$, when $\xi > 1/z_-$, the density of counterions will be very large near the surface of the macromolecule. These counterions are bounded to the macromolecule: besides the diffuse screening cloud of ions around the macromolecule, there is also a thin layer of condensed counterions very near to the surface of the cylinder.

This counterion condensation effect can be studied quantitatively in the mean field approximation, since an analytical solution of the nonlinear Poisson–Boltzmann equation in the cylindrical geometry is available. For a 1:1 electrolyte, this solution was found by [McCoy, Tracy and Wu 1977], in a different context, in relation to the correlation functions of the two-dimensional Ising model. Later on, [Widom 1997] developed the solution for the asymmetric cases 2:1 and 1:2, and [Tracy and Widom 1998] studied the short-distance asymptotics of the solution and solved the problem of connecting the large-distance and the short-distance behaviors of the solution. The consequences of this mathematical work to the screening of cylindrical macromolecules were reported by [McCaskill and Fackerell 1988], [Tracy and Widom 1997] and [Trizac and T  lez 2006]. A more extensive study is

presented in [Téllez and Trizac 2006]. We summarize here some of the main findings of that work.

The short-distance behavior of the potential can be obtained by a physical argument. Very close to the charged cylindrical macromolecule, one would expect the potential to be the bare Coulomb potential $-2A \ln r + \text{constant}$, with A some constant related to the charge of the macromolecule. By replacing this ansatz into Poisson–Boltzmann equation (1.3) one can compute systematically the following terms of the short-distance expansion, to find [Tracy and Widom 1998, Téllez and Trizac 2006, Trizac and Téllez 2007]

$$y(r) = -2A \ln \hat{r} + 2 \ln B - 2 \ln \left[1 - \frac{B^2 \hat{r}^{2-2A}}{16(1-A)^2} \right] + O(\hat{r}^{2+2A}). \quad (3.1)$$

We specialize here in the 1:1 electrolyte. For the general case of a $z_+ : z_-$ electrolyte, see [Trizac and Téllez 2007]. A and B are some constants of integration. The constant A can be related to the charge density of the electrolyte by writing the first boundary condition (1.7)

$$\xi = A - \frac{(2-2A)(\kappa a)^{2-2A} B^2}{16(1-A)^2 - B^2(\kappa a)^{2-2A}}. \quad (3.2)$$

From the previous section, we already know the large-distance behavior of the potential, it is the screened potential (2.3)

$$y(r) \sim 4\lambda K_0(\hat{r}), \quad (3.3)$$

where λ is some constant related to the renormalized charge by

$$\xi_{\text{ren}} = \hat{a} K_1(\hat{a}) \lambda / 2. \quad (3.4)$$

By using the explicit analytical solution of the nonlinear Poisson–Boltzmann equation from [McCoy, Tracy and Wu 1977] and [Widom 1997], [Tracy and Widom 1998] where able to solve the connection problem of relating the constants of integration from the short-distance behavior A and B , to the one of the large-distance behavior λ . To satisfy the boundary condition $y'(r) \rightarrow 0$ when $r \rightarrow \infty$, the constants A and B need to satisfy

$$B = 2^{3A} \frac{\Gamma\left(\frac{1+A}{2}\right)}{\Gamma\left(\frac{1-A}{2}\right)}, \quad (3.5)$$

where Γ is the gamma function, and, A and λ need to satisfy

$$\lambda = \frac{1}{\pi} \sin\left(\frac{\pi A}{2}\right). \quad (3.6)$$

The first physical consequence of these relations, is that we can obtain an analytical expression for the renormalized charge, by combining equations (3.2), (3.4) and (3.6). In the simplest situation, when $a = 0$, this gives, $A = \xi$ and

$$\xi_{\text{ren}} = \frac{2}{\pi} \sin \frac{\pi \xi}{2}. \quad (3.7)$$

(b) Counterion condensation

The previous discussion, and in particular equation (3.1) are only valid provided that $A < 1$. Indeed, if $A = 1$, equation (3.1) becomes singular: the last term becomes of the same order as the second, and besides, the constant B from equation (3.5) becomes undefined. This is the mathematical signature of the counterion condensation phenomenon. Notice that for $a = 0$, the constant A is the linear charge of cylinder $A = \xi$, and the value $\xi_{\text{Manning}} = 1$ is precisely the threshold for counterion condensation discussed earlier.

For a cylinder with nonzero radius $a \neq 0$, notice that, using equation (3.2), the threshold $A = \xi_{\text{Manning}} = 1$ corresponds for the linear charge to the threshold

$$\xi_c = 1 + \frac{1}{\ln \hat{a} + C}, \quad (3.8)$$

with $C = \gamma - 3 \ln 2 \simeq -1.502$, with γ the Euler constant. Note that there is a negative logarithmic correction in the radius a of the cylinder to the Manning value $\xi_{\text{Manning}} = 1$ for the threshold for condensation: $\xi_c \leq 1$.

To extend the solution beyond the condensation threshold, [Tracy and Widom 1998] suggested to write A as a complex number $A = 1 - i\mu/2$. Replacing into equation (3.1), the short-distance expansion of the potential now reads

$$y(r) = -2 \ln \hat{r} - 2 \ln \frac{\sin(-2\mu \ln \hat{r} - 2\mu C)}{4\mu}. \quad (3.9)$$

The constant μ can be expressed in terms of the bare linear charge density ξ by using the first boundary condition (1.7), and connected to the large-distance expansion of the potential and the renormalized charge by means of equation (3.6), replacing $A = 1 - i\mu/2$, for details see [Téllez and Trizac 2006].

Notice the first term of expansion (3.9) : $-2 \ln \hat{r}$. It is the bare Coulomb potential of a charged line with linear charge density $\xi_{\text{Manning}} = 1$. This is a characteristic of the counterion condensation phenomenon. At intermediate distances of the charged cylinder, one “sees” a cylinder with an effective charge $\xi_{\text{Manning}} = 1$, if the bare charge exceeds the threshold value ξ_c . The second term of equation (3.9) can become very large in the close proximity of the cylinder. This second term represents the thin layer of condensed counterions located at the surface of the cylinder. Figure 2, shows a plot of the potential close to the cylinder, and compares it to the bare term $-2 \ln \hat{r}$.

4. Concluding remarks

To summarize and conclude the review presented here, we would like to stress the differences between the different linear charges densities that we presented for cylindrical macromolecules: renormalized charge, Manning charge, threshold charge for counterion condensation.

The renormalized charge characterizes the behavior of the potential far from the charged macromolecule. At those large distances, $r \gg \kappa^{-1}$, the potential exhibits an exponential decay. The prefactor of this exponential decay is proportional to the renormalized charge, as shown in equation (2.3).

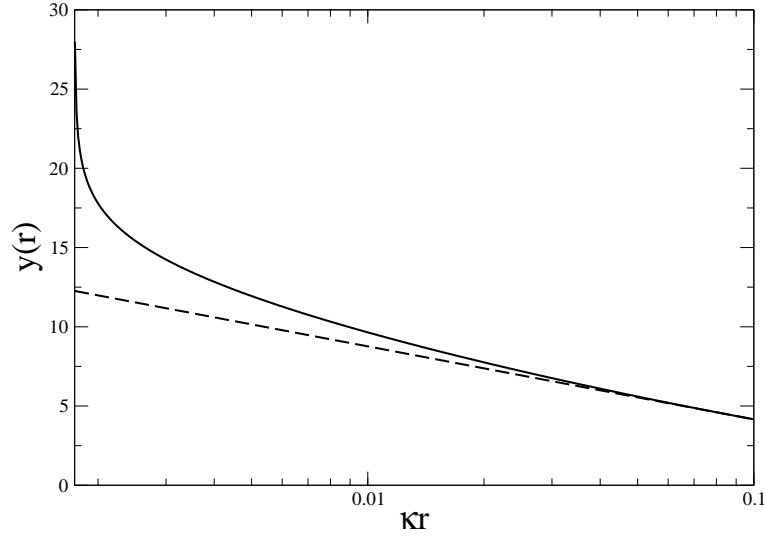


Figure 2. Short-distance expansion of the potential (3.9) (thick line) compared to $-2\ln(\hat{r}/(4\mu))$ (dashed line). Parameter $\mu = 0.2$.

At short distances, there are two possible behaviors, depending on the value of the bare linear charge density ξ compared to the threshold value ξ_c given by equation (3.8). If $\xi < \xi_c$, the potential behaves as given by equation (3.1). It is a bare Coulomb potential with a prefactor given in terms of the bare charge of the macromolecule. If $\xi > \xi_c$, the counterion condensation takes place. The short-distance behavior of the potential is given by equation (3.9). A thin layer of counterions is bound to the surface of the cylinder, which makes the potential very large in that region. Beyond this layer, the potential behaves as $-2\xi_{\text{Manning}}\ln r$: the bare Coulomb potential for a charged cylinder but with an effective charge $\xi_{\text{Manning}} = 1$, the Manning charge for counterion condensation, see figure 2. Notice that if the radius of the cylinder $a \neq 0$, the Manning value differs from the threshold value: $\xi_{\text{Manning}} > \xi_c$.

The counterion condensation phenomenon can be only noticed at close proximity of the charged cylinder, by the change of the short-distance behavior of the potential from (3.1) to (3.9). At large distances, the potential is always given by (2.3), regardless if the counterion condensation has taken place or not. When $\xi = \xi_c$, no singularity appears in equation (2.3), nor in the renormalized charge ξ_{ren} which characterizes only the large-distance behavior of the potential. Also, notice that $\xi_{\text{ren}} \neq \xi_{\text{Manning}}$ and $\xi_{\text{ren}} \neq \xi_c$. This has caused some confusion in the past, since in the original work of [Manning 1969], in the condensed phase, the diffuse screening cloud of the remaining uncondensed counterions around the charged cylinder was treated using the linear Poisson–Boltzmann equation and using an effective charge of the cylinder given by $\xi_{\text{Manning}} = 1$ to account for the counterion condensation. It turns out that this picture is not completely correct, since besides the counterion condensation, there are also additional nonlinear effects in the uncondensed cloud that are responsible for an additional charge renormalization. As a result

$\xi_{\text{ren}} \neq \xi_{\text{Manning}}$. For example, in the limiting case $a = 0$, from equation (3.7), we obtain $\xi_{\text{ren}} = 2/\pi \simeq 0.63662 < \xi_{\text{Manning}} = 1$.

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References

- [Alexander et al. 1984] Alexander, S., Chaikin, P. M., Grant, P., Morales, G. J. and Pincus, P. 1984 Charge renormalization, osmotic pressure, and bulk modulus of colloidal crystals: Theory. *J. Chem. Phys.* **80** 5776.
- [Bocquet et al. 2002] Bocquet, L., Trizac, E. and Aubouy, M. 2002 Effective charge saturation in colloidal suspensions. *J. Chem. Phys.* **117** 8138.
- [Chapman 1913] Chapman, D. L. 1913 A contribution to the theory of electrocapillarity. *Philos. Mag.* **25** 475.
- [Debye and Hückel 1923] Debye, P. and Hückel E. 1923 The theory of electrolytes. I. Lowering of freezing point and related phenomena. *Phys. Z* **24** 185.
- [Derjaguin and Landau 1941] Derjaguin, B. and Landau, L. 1941 Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physico Chemica URSS* **14**, 633.
- [Gouy 1910] Gouy, G. L. 1910 Sur la constitution de la charge électrique a la surface d'un électrolyte. *J. Phys.* **9**, 457.
- [Manning 1969] Manning, G. S. 1969 Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions I. Colligative Properties. *J. Chem. Phys.* **51** 924
- [McCaskill and Fackerell 1988] McCaskill, J. S., and Fackerell, E. D. 1988 Painlevé solution of the Poisson–Boltzmann equation for a cylindrical polyelectrolyte in excess salt solution. *J. Chem. Soc. Faraday Trans. 2* **84** 161
- [McCoy, Tracy and Wu 1977] McCoy, B. M., Tracy, C. A., and Wu, T. T. 1977 Painlevé functions of the third kind. *J. Math. Phys.* **18** 1058.
- [Oosawa 1971] Oosawa, F. 1971 *Polyelectrolytes*. Dekker, New York.
- [Overbeek and Verwey 1948] Verwey, E. J. W. and Overbeek, J. T. G. 1948 *Theory of the stability of lyophobic colloids*. Elsevier.
- [Shkel et al. 2000] Shkel, I. A., Tsodikov, O. V. and Record, M. T. 2000 Complete asymptotic solution of cylindrical and spherical Poisson–Boltzmann equations at experimental salt concentrations. *J. Phys. Chem. B* **104** 5161.
- [Téllez and Trizac 2003] Téllez, G., and Trizac, E. 2003 Density functional theory study of the electric potential saturation: Planar geometry. *Phys. Rev. E* **68** 061401.
- [Téllez and Trizac 2004] Téllez, G. and Trizac, E. 2004 Non-linear screening of spherical and cylindrical colloids: the case of 1:2 and 2:1 electrolytes. *Phys. Rev. E* **70** 11404.
- [Téllez and Trizac 2006] Téllez, G., and Trizac, E. 2006 Exact asymptotic expansions for the cylindrical Poisson–Boltzmann equation. *J. Stat. Mech.* P06018.
- [Tracy and Widom 1997] Tracy, C. A., and Widom, H. 1997 On exact solutions to the cylindrical Poisson–Boltzmann equation with applications to polyelectrolytes. *Physica A* **244** 402.
- [Tracy and Widom 1998] Tracy, C. A., and Widom, H. 1998 Asymptotics of a Class of Solutions to the Cylindrical Toda Equations. *Comm. Math. Phys.* **190** 697.
- [Trizac et al. 2002] Trizac, E., Bocquet, L. and Aubouy, M. 2002 A simple approach for charge renormalization of highly charged macro-ions. *Phys. Rev. Lett.* **89** 248301.
- [Trizac et al. 2003] Trizac, E., Aubouy, M., and Bocquet, L. 2003 Analytical estimate of effective charges at saturation in Poisson–Boltzmann cell models. *J. Phys.: Condens. Matt.* **15** S291.
- [Trizac and Téllez 2006] Trizac, E., and Téllez, G. 2006 Onsager-Manning-Oosawa Condensation Phenomenon and the Effect of Salt. *Phys. Rev. Lett.* **96** 038302
- [Trizac and Téllez 2007] Trizac, E. and Téllez, G. 2007 Preferential interaction coefficient for nucleic acids and other cylindrical polyions. *Macromolecules* **40**(4) 1305.

- [Widom 1997] Widom, H. 1997 Some Classes of Solutions to the Toda Lattice Hierarchy.
Comm. Math. Phys. **184** 653.